

Effect of Plasticizer Concentration on Microstructural and Dielectric Properties of Polymer Composite Electrolyte

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Abstract

A series of plasticized composite polymer electrolytes (PCPEs) based on Poly (ethylene oxide) + NaClO₄ dispersed with SnO₂ as the filler and plasticized by an organic solvent Poly (ethylene glycol) has been studied. The changes in the sample microstructure, variation of structural disorder parameters and dielectric properties as a function of plasticizer concentration have been investigated. The X-ray line profile analysis method of Variance and Fourier analysis techniques have been adopted to calculate different microstructural parameters *i.e.*, crystallite size, r. m. s. strain, variation of interlayer spacing and fraction of planes affected by such disorder. The changes occurring in these microstructural parameters on plasticizer addition have been studied and correlated with the electrical conductivity of the material. The low frequency dielectric constant increases with the increment in plasticizer concentration. The dielectric loss data shows that the relaxation peak shifts towards the higher frequency side on addition of plasticizer suggesting the decrease in relaxation time *i.e.*, segmental motion is speed up. A. C. conductivity spectrum obeys the Jonscher's power law feature.

Keywords

Polymer Composite Electrolyte; Dielectric Properties; Microstructural Parameters; Crystallite size

Introduction

Ionically conducting and dimensionally stable polymer film better known as the solid polymer electrolytes (SPEs) has now a history of over decades initiated after startling revelations of ionic conduction in polymers by Wright *et al.*. Later Armand highlighted the scope of practical applicability of such conducting films and emphasized a promising future due to advantages over liquid electrolytes leading to further research and development in this area. Henceforth, many works (MacCallum *et al.* 1987, Shriver *et al.* 1995, Bruce *et al.* 1995 and Gray *et al.* 1995) have been reported in this technologically important subject area. Development aspects are required for various types of modifications in SPEs resulting in

preparation and characterization of a wide variety of materials such as composite polymer electrolytes (CPEs) (Vincent *et al.* 1987, Weston *et al.* 1982, Wiezorek *et al.* 1998, Hashmi *et al.* 2000 and Croce *et al.* 2000), plasticized polymer electrolytes (Chandra *et al.* 1994, and Macfarlane *et al.* 1995), co-polymerized composite electrolytes (Reddy *et al.* 1999 and Kumar *et al.* 2001), plasticized composite polymer electrolyte (PCPEs) (Yang *et al.* 1995 and Leo *et al.* 2002) and now polymer nanocomposite electrolyte (PNC) films (Pradhan *et al.* 2005 and Aranda *et al.* 1992). Various aspects of SPEs such as dielectric properties, microstructure, phase analysis, thermal properties, stability and possibility of device applications have been studied and evaluated. However, the priority of all such studies has been to optimize the material properties leading to device applications (MacCallum *et al.* 1987, Shriver *et al.* 1995, Bruce *et al.* 1995 and Gray *et al.* 1995).

The most widely studied polymer host for electrolyte is polyethylene oxide (PEO). It has a liquid-solid coexistence regime in the phase diagram of PEO-metal system above ambient temperature and other desirable properties such as electron donicity, low glass transition temperature, suitable static permittivity factoring ion solvation. Several monovalent (Ruizhitzky *et al.* 1990 and Fantuex *et al.* 1987), divalent (Rao *et al.* 1994 and Vossage *et al.* 1993), trivalent salts have been dissolved in PEO leading to a variety of solid polymer electrolytes. Extensive reviews describing different aspect of materials formation and analysis existed in literature (Vincent *et al.* 1987, Thakur *et al.* 2006, Hickner *et al.* 2010 and Pradhan *et al.* 2011).

Fontanella *et al.* discussed the low frequency dielectric behavior of PEO, PPO (Polypropylene oxide) and ion containing PEO and PPO salt complex and then reviewed that the dielectric parameters are both

frequency and temperature dependent for pure PEO and PPO. The change in the real and imaginary part of dielectric constant has been observed for different type of salt in solid polymer electrolyte. The dielectric and conductivity spectrum of polyethylene oxide complex with sodium salt has been investigated by Shriver *et al.* in the radio and microwave frequency region. Later Mellander *et al.* studied the electrical and dielectric properties of ionically conducting polymer electrolyte (*i. e.*, poly (propylene glycol) complex with salt trifluoromethanesulfonate) in order to get additional information on ion conduction mechanism in a wide frequency range. Elisasson *et al.* studied the dielectric properties of some Ag ion conducting polymer electrolyte. They studied the dielectric relaxation behavior and observed two loss peaks, a primary peak that may be attributed to the ion pair and low intensity peak only visible at low salt concentration that is assumed to be the relaxation due to the polymer chain. The dielectric response behavior of some polymer gel electrolyte system has been investigated by Jayathilake *et al.*. Bandre *et al.* reported the dielectric response of the Li ion conducting plasticized polymer electrolyte in a wide frequency range and temperature. Recently, Stephan *et al.* studied the composite polymer electrolytes (CPEs) in view of their electrochemical and physical properties for the applications in lithium batteries. Moreover Rupp *et al.* reported the Polymer/ionic liquid composites as solvent-free electrolytes for lithium batteries.

The crystal structure of modified PEO has been first reported by Takahasi *et al.*. It has been found that in pure PEO, sharp and intense diffraction peak occurs at $2\theta \sim 19^\circ$ and 23° confirming its crystalline nature. Takahasi *et al.* have indexed the plane around 19° as the [100] plane. Studies related to correlation of the physical properties of SPEs and changes occurring therein on composite formation/co-polymerization/plasticization have always been a gray area. Microstructural changes in the polymer host matrix on salt/filler/plasticizer addition controls and governs the electrical conduction properties. In view of this, studies related to structural aspects in SPEs are of much significance to get an insight into the changes occurring in its electrical conductivity on ceramic dispersion or plasticization.

We have reported previously, the synthesis conditions and electrical analysis of plasticized composite polymeric system having general formula: $(\text{PEO})_{25}\text{-NaClO}_4 + 10\text{wt.}\%\text{SnO}_2 + x\text{wt.}\%\text{PEG}_{200}$ (Pradhan *et al.* 2005). In this paper, we report the effect of plasticizer concentration on the microstructural disorder

parameters and dielectric properties of the above system. Effects of plasticizer addition on different structural/microstructural parameters such as crystallite size, r. m. s. strain, layer disorder, interlayer spacing have been analyzed using X-ray line profile analysis and the changes correlated to electrical conductivity. The role of plasticizer concentration on dielectric permittivity, tangent loss, a. c. and d. c conductivity at room temperature has also been studied.

Theoretical Background

X-ray diffraction (XRD) peaks and changes occurring therein on addition of a new component in to the matrix provide precise and reliable information on microstructural aspect of a system. X-ray diffraction peaks broaden when the crystal lattice become imperfect. So a broadening in the XRD peaks may occur due to several causes such as (i) finite coherent length (small crystallite size), (ii) micro strains in the crystallite and (iii) stacking disorder.

The variance (W) of the x-ray profile is a measure of line broadening (Langford *et al.* 1965 and Wilson *et al.* 1962) and given by $W = W_p + W_s + W_d$, where W_p is the factor corresponding to crystallite size, W_s is the factor corresponding to lattice strain and W_d is the factor corresponding to layer disorder. Substituting the results of Mitra *et al.*, Mitra and Bhattacharjee *et al.* we have

$$W = \frac{\alpha(2\theta)\lambda}{2\pi^2 p' \cos\theta} + \frac{S\lambda^2}{\cos^2\theta} \quad (1)$$

where

$$S = \frac{\langle e^2 \rangle - \beta_D^2 / \pi^2}{d^2} \quad (2)$$

and

$$\frac{1}{p'} = \frac{1}{p} + \frac{\beta_D}{d} \quad (3)$$

Where $\langle e^2 \rangle$ is the mean square strain, d is the mean interplaner spacing, θ is the corresponding Bragg's angle for wavelength λ , p is crystallite size, γ is the probability of the reflecting planes having defects of the type of variable interlayer spacing. $\alpha(2\theta)$ represent total angular range in 2θ scale over which the measurements are made, l is the order of reflection. In equation (3) p' denote the apparent particle size, p is true particle size and β_D is the integral width of the defect profile. Taking equation (1), the plot of $W(2\theta)$ with respect to $\alpha(2\theta)$ will be linear and slope will give apparent particle size p' and the intercept will be $\frac{\langle e^2 \rangle - \beta_D^2 / \pi^2}{d^2}$. If the faulting is dominating, the intercept will be on negative side of the ordinate, otherwise the intercept will be positive side of the

ordinate. The true particle size p is determined using the Fourier line profile analysis technique. By knowing the value of p and p' we can calculate the value of β_D . If ' g ' be the mean fractional change in the interlayer distance in any given direction and γ be the transition probability i. e. the proportion of the planes affected by disorder of all the sample has been calculated from [100] reflection. The value of g and γ can be determined from

$$g = (1/\pi l) \cot^{-1} (\pi \Delta / \beta_D) \quad (4)$$

$$\& \gamma = \beta_D / \sin^2(\pi l g) \quad (5)$$

Where β_D is the integral width of the defect profile and Δ is the distance of the peak from the centroid of the diffraction profile.

Materials Preparation and Characterization

Plasticized composite polymer electrolyte films of different plasticizer concentration were prepared by a standard solution cast technique. The PCPEs composition may be expressed as: $(\text{PEO})_{25}\text{-NaClO}_4 + 10\text{wt.}\%\text{SnO}_2 + x\text{wt.}\%\text{PEG}$ ($x = 0, 10, 20, 30$ and 50). The x-ray diffraction (XRD) pattern of the plasticized polymer films was recorded at room temperature using x-ray diffractometer (Philips, Model 1710) with $\text{CuK}\alpha$ radiation. The details preparation and characterization technique carried out has been reported by us elsewhere (Pradhan *et al.* 2005). An analysis of the dielectric properties of PCPE films has been carried out using impedance spectroscopy on application of a small a. c. signal across the sample cell with blocking electrode. The impedance measurements were carried out using a computer-controlled impedance analyzer (HIOKI LCR Hi TESTER Model: 3532) in the frequency range of 100 Hz to 1 MHz. The dielectric properties (permittivity and tangent loss factor) have been observed as a function of frequency and temperature. A. C. conductivity has been evaluated from dielectric data in accordance with the relation: $\sigma_{ac} = \omega \epsilon_0 \epsilon_r \tan \delta$ where $\epsilon_r = C/C_0$ is the relative permittivity, $\tan \delta$ = tangent loss factor, C_0 = vacuum capacitance of the cell.

Results and Discussion

Figure 1 shows the X-ray diffraction pattern of the PCPEs at room temperature in the 2θ range $8\text{--}30^\circ$ reported by us (Pradhan *et al.* 2005). The peak around 19° and 23° are the characteristic peaks of PEO. It was observed that after complexation with an alkali salt, the $20 \sim 23^\circ$ reflection is slightly affected whereas $20 \sim 19^\circ$ peak is significantly affected. Therefore the angle $20 \sim 19^\circ$ should be the preferred crystallographic

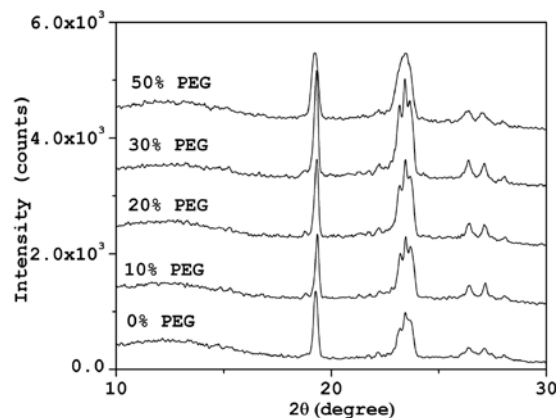


FIG. 1 X-RAY DIFFRACTION PATTERNS OF PLASTICIZED COMPOSITE POLYMER ELECTROLYTES.

direction where an interaction of PEO and salt takes place. Similar observations have been reported by Zain *et al.*. On addition of filler and plasticizer, due to the interaction of filler and plasticizer with the polymer-salt complex, changes in the peak position peak intensity and peak width has been observed. Takahashi *et al.* has reported the structure of PEO. From their report about the structure of PEO, it was observed that the chain to chain distances are along the [100] direction and have very weak inter chain forces as compared to the strong intra chain forces.

When plasticizers are added, these weak bonds are further weakened and the variability of disorder increases. Hence, the disorder parameters along that direction have been calculated in the present study.

To calculate the different microstructural parameters, x-ray line profile analysis of the [100] reflection of the composite polymer electrolyte (CPE) and sample containing different concentration of plasticized composite polymer electrolyte (PCPE) were analyzed by the variance method. As the method of variance is sensitive to variation near the tails of the line profile, the variance analysis was carried out after carefully correcting the background. The variance – range ($W(2\theta)$ vs. $\alpha(2\theta)$) plot for 0% PEG is shown in the Figure 2 as representative.

Similar variations have been observed for all other compositions. The linearity of the variance range plot establishes the correctness of the background correction. From the slope of the plot, the apparent crystallite size (p') has been calculated. It has been found that the intercept is along the negative side of the ordinate, which indicates that the faulting disorder plays a more predominant role than the strain. True particle sizes were also calculated from the Fourier line profile analysis following the Warren and

Averbach (Warren *et al.* 1950, Marinkovic *et al.* 2001 and Crist *et al.* 1979) method using software package XPowder (Martin 2004). As expected from equation (3), the crystallite size calculated from Fourier method (p) for all these samples were always found to be higher than that of the crystallite size calculated by the variance method. It is very interesting to note that the dependence of crystallite size on plasticizer concentration as obtained from variance as well as the Fourier method has one to one correspondence as shown in Figure 3. With the addition of plasticizer (PEG), it is observed that there is a decrease in crystallite size values.

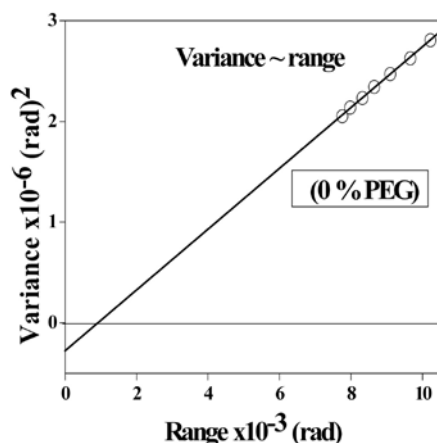


FIG. 2 VARIANCE RANGE PLOT OF [100] PLANE OF COMPOSITE POLYMER ELECTROLYTE (0 % PEG)

Figure 4 shows the variation of r. m. s. strain as a function of plasticizer concentration. It has been noticed that the r. m. s. strain monotonically increases with increment in plasticizer concentration of PEG. The rise in the r. m. s. strain may be due to the higher disorder corresponding to the random and local lattice distortion (Crist *et al.* 1979). Figure 5 shows the variation of variability of interlayer spacing (g) and fraction of planes affected by layer disorder type defects (γ) as a function of plasticizer concentration. It has been noticed that the fraction of planes affected by such defects decreases on addition of plasticizer. On the other hand the change in the variability of interlayer spacing (g) increases with increment in plasticizer concentration. Thus both the variation of $\langle e^2 \rangle^{1/2}$ and ' g ' point to the fact that disorder in the structure increases significantly on addition of PEG.

The d. c. electrical conductivity of the plasticized composite polymer electrolyte has been evaluated from complex impedance spectrum data. Figure 6 shows the variation of electrical (d. c.) conductivity of $(\text{PEO})_{25}\text{NaClO}_4 + 10\text{wt}\%\text{SnO}_2 + x\text{wt}\%\text{PEG}$ as a function of plasticizer concentration, which have been reported

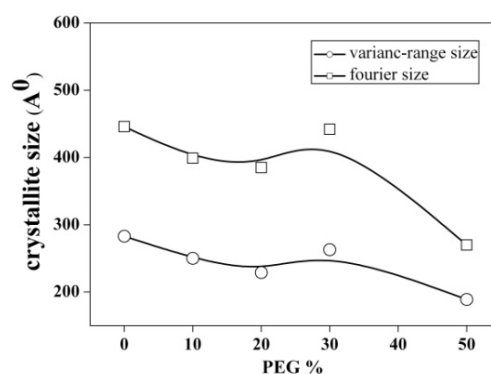


FIG. 3 PLOT OF THE CRYSTALLITE SIZE OBTAINED BY THE METHOD OF VARIANCE (p') AND FOURIER METHOD (p) AS A FUNCTION OF PLASTICIZER CONCENTRATION

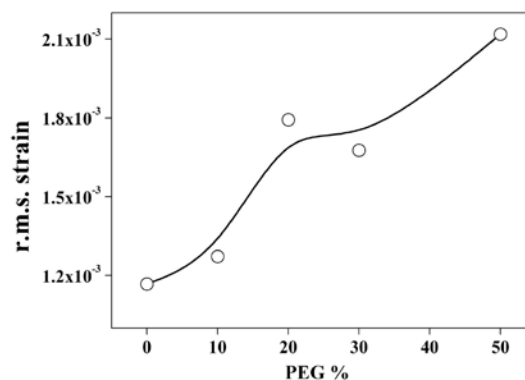


FIG. 4 VARIATION OF r. m. s. strain $\langle e^2 \rangle^{1/2}$ AS A FUNCTION OF PLASTICIZER CONCENTRATION

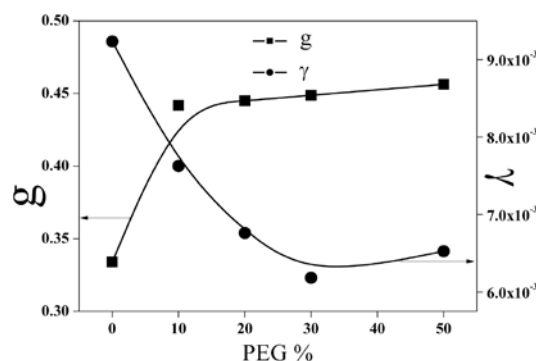


FIG. 5 VARIATION OF G AND γ AS A FUNCTION OF PLASTICIZER CONCENTRATION

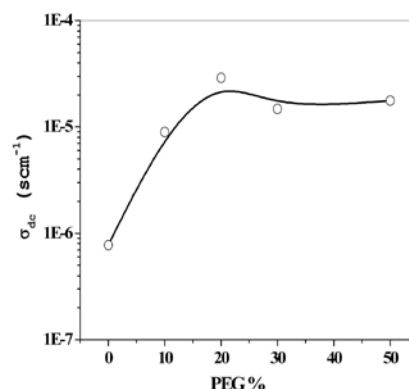


FIG. 6 VARIATION OF d. c. CONDUCTIVITY AS A FUNCTION OF PLASTICIZER CONCENTRATION AT ROOM TEMPERATURE

by us (Pradhan *et al.* 2005). The d. c. electrical conductivity increases with increment in plasticizer concentrations and follows a plateau on and above 20% PEG. There is an enhancement in electrical conductivity by more than one order of magnitude for films containing 20wt. % of PEG at room temperature. Since the d. c. conductivity is nearly constant on and above 20% PEG addition, it is expected that the value of the conductivity will remain constant even if further addition of plasticizer more than 50%. So we did not tried for more than 50% plasticizer addition. Similar type of variation of electrical conductivity has also been reported by us in plasticized polymer nanocomposite electrolytes (Pradhan *et al.* 2011).

For polymer-salt-ceramics complex of polymer composites system, the plasticizer PEG₂₀₀ has been added. The plasticizer molecules are relatively small in size as compared to the polymer molecules. Hence the plasticizer molecules penetrate in to the polymer matrix and establish attractive forces between plasticizer molecules and PEO chain segments. This attractive force reduces the cohesive forces between the polymer chains. Possibly this is responsible for increase in the g value but decrease in the γ value. Similar variations have been observed by Mitra *et al.* and Sao *et al.*. It is generally accepted that ion transport in polymer electrolytes occur primarily through amorphous region of the complex. The amorphous regions are more disorders as compared to the crystalline regions. On addition of plasticizer there is an increase in the amorphous content and ultimately the disorderness in the system. The increase in the disorder parameters are well reflected in terms of increase in the variability of interlayer spacing, the r. m. s. strain and decrease in the crystallite size. Thus there is the increase in the electrical conductivity with the addition of plasticizer, which is well correlated with the change in the microstructural and disorder parameters.

Figure 7 shows the variation of relative dielectric constant with frequency for different PEG concentration at room temperature. In all the cases, it has been found that there is a sharp decrease in the ϵ_r value in the lower frequency region and a frequency independent value on and above 1 kHz is shown. It is seen that with addition of plasticizer ϵ_r value increases in the lower frequency region and nearly same in the higher frequency region. The high permittivity in the plasticized system can be attributed to the localization of charge carriers (Baskaran *et al.* 2004). In the lower frequency region the larger value of the dielectric

constant (ϵ_r) may be the contribution of moving ions causing the higher ionic conductivity, resulting in electrochemical double layers at the electrodes. This type of conduction often makes it difficult or impossible to detect dipole relaxation due to permanent dipoles (MacCallum *et al.* 1987).

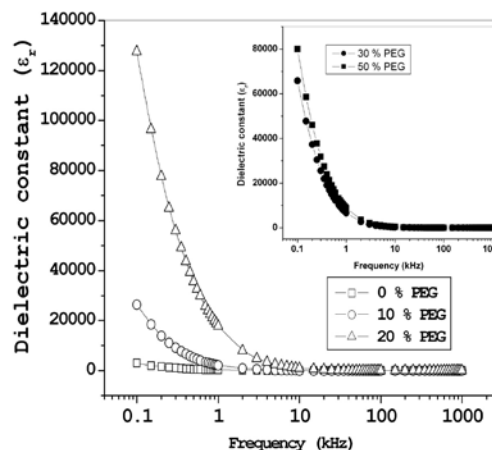


FIG. 7 VARIATION OF RELATIVE DIELECTRIC CONSTANT (ϵ_r) WITH FREQUENCY FOR DIFFERENT CONCENTRATIONS OF PEG AT ROOM TEMPERATURE

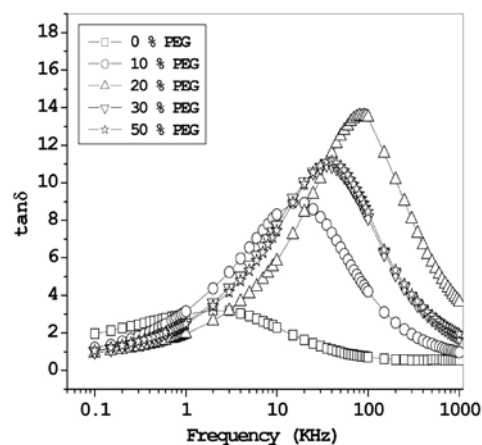


FIG. 8 VARIATION OF DIELECTRIC LOSS ($\tan\delta$) WITH FREQUENCY FOR DIFFERENT CONCENTRATIONS OF PEG AT ROOM TEMPERATURE

Figure 8 shows the variation of tangent loss with frequency for different concentration of PEG at room temperatures. The loss spectra are characterized by peak appearing at a characteristic frequency for different plasticizer concentration. The appearance peak in the loss spectra suggests the presence of relaxing dipoles in all the samples. The peak frequency shifting towards the higher frequency side with plasticizer addition and after 30 % of PEG, it is nearly a constant value. The relaxation processes, the glass transition temperature can be assigned only to the amorphous component. In semi crystalline polymer, the amorphous component is constrained by the crystal and the glass transition is much broader in a

semi-crystalline polymer than that in amorphous polymer. The dielectric loss process can be assigned by the relaxation processes due to glass transition of the amorphous component of the polymer (Gedde *et al.* 1995). From the above figure, it is found that the relaxation shifts toward the high frequency side. This can be explained that the diluent molecules (PEG₂₀₀) are small and mobile; and they effectively increase the available free volume for segmental motion and speed it up i. e. decreasing the relaxation time (Boyd *et al.* 1985).

Figure 9 shows the variation of a. c. conductivity with frequency for different concentration of plasticizer (PEG) at room temperature. From the figure; it has been found that the conductivity spectrum consists of three different regions; the low frequency dispersion which is followed by a medium frequency independent plateau and frequency dispersion at the high frequency region. The dispersion of conductivity in the lower frequency region is more prominent with increase in PEG concentration. The lower frequency a. c. conductivity may be attributed to the electrode polarization effect (space charge polarization at the blocking electrode) resulting in the drop of conductivity (Perez *et al.* 1998). It has been observed that with increase in plasticizer concentration the low frequency dispersion is more prominent. At moderate frequency region, the frequency independent plateau like region is assigned to the d. c. conductivity of the material. The high frequency part of the curve corresponds to the bulk relaxation phenomena (Furlani *et al.* 1998). It is observed that there exists a transition of frequency independent d. c. conductivity to frequency dependent a. c. conductivity which shifts towards the higher frequency side with addition of plasticizer. The suppression of frequency dependent a. c. conductivity at the higher frequency side with increase in plasticizer concentration has been noticed.

The high frequency dispersion in the higher frequency side is maximum compared to CPE than PCPE and decrease with plasticizer addition.

In this case the behavior of conductivity spectrum can be explained by using the Jonscher's power law (Jonscher *et al.* 1977) at constant temperature can be expressed as

$$\sigma(\omega) = \sigma_{dc} + A\omega^n, \quad 0 < n < 1$$

where σ_{dc} is the frequency independent conductivity $\omega \rightarrow 0$, A is the temperature dependent pre-factor and n is the frequency exponent. This equation is known as a. c. universal law as this equation is found to be satisfying and describing an a. c. response of different types of materials.

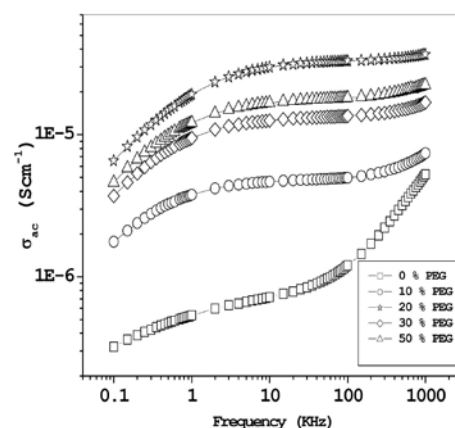


FIG. 9 VARIATION OF a. c. CONDUCTIVITY WITH FREQUENCY FOR DIFFERENT CONCENTRATIONS OF PEG AT ROOM TEMPERATURE

Conclusions

A plasticized composite polymer electrolyte having heterogeneous combination (polymer-salt-filler-plasticizer) has been studied. The effect of plasticizer concentration on the microstructural disorder parameters like crystallite size, r. m. s. strain, variation of interlayer spacing and fraction of planes affected by such defects etc. have been investigated using Variance and Fourier method of line profile analysis. The values of the crystallite sizes obtained by the Fourier method were higher than that obtained by the variance method. The fraction of planes affected by defects decreased on addition of plasticizer; on the other hand, the change in the interlayer spacing increased on addition of plasticizer and attained a constant value at higher plasticizer concentrations. The changes in the disorder parameters were well correlated with the changes in the electrical conductivity. The low frequency dielectric constant increased with rise in plasticizer concentrations. The loss tangent spectra showed a dielectric relaxation peaks for all plasticizer concentrations. Jonscher's power law has been used to explain the frequency dependent a.c. conductivity.

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